Study the corrosion inhibition of carbon steel metal using pure curcumin in seawater solution

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ABSTRACT:*The corrosion inhibition of carbon steel in seawater solution (3.5%NaCl and DMSO) by pure curcumin has been studied at temperature range (298-328K) and different concentrations ($2.7*10^{-6}$,$1.3*10^{-5}$,$2.7*10^{-5}$,$3.2*10^{-5}$M) using potentiostatic techniques. The results showed that the best corrosion inhibition efficiency was obtained with$2.7*10^{-5}$Mpure curcumin concentration which reach to 77.5% at 298K.The corrosionrate increase with increase temperature at all purecurcuminconcentrations.Thecorrosion rate decreasewith purecurcuminconcentration increaseup to $2.7*10^{-5}$Mthen with increasing pure curcumin concentration than $2.7*10^{-5}$M the corrosion ratewill be increase. Apparent activation energy, Arrhenius factor, free energyΔG^*, enthalpy ΔH^* and entropy ΔS^* for corrosion processeswere calculated. The inhibition mechanism according to adsorption of pure curcumin molecules in the interface metal/solution and Langmuir adsorption isotherm type were applied.*

KEYWORDS:*Carbon steel,Curcumin, Sea water, Corrosion, Inhibitors.*

I. INTRODUCTION

Corrosion is a natural phenomenon involving the reversion from metallic to compound state. The corrosion occurs because of the natural tendency for most metals to return to their natural state. It cannot be avoided, but it can be controlled and prevented using the suitable preventive measures such as alloying, cathodicprotection, anodic protection, protective coating and application of inhibitors, etc [1].

Among the various methods to avoid or prevent destruction or degradation of metal surface, the usage of corrosion inhibitors is one of the best known methods of corrosion protection in engineering industry.This method is following stand up due to low cost and practice method. [2-4].

Organic compounds with heteroatoms such as oxygen, nitrogen, sulfur and phosphorus are the most reported inhibitors for the metal corrosion. Organic inhibitors act by the adsorption on the metal surface to form a layer and decrease the corrosion rate [5-8].

Turmeric rhizomes belong to Zingiberaceae family that is distributed mostly in tropical and subtropical areas. Zingiberaceae species have common uses in the Southeast Asian countries such as food flavor, traditional medicine, and source for certain dyes [9-11].

Curcumin is one of theenvironmentally friendly corrosion inhibitors,chemical name (CUR, 1), 1,7-bis(4-Hydroxy-3-methoxyphenl)-1,6-heptadiene-3,5-dione (figure 1)and it is the major active compound found in turmeric[12].

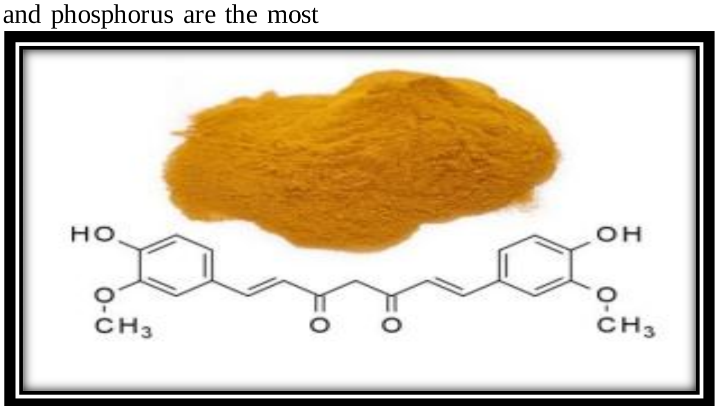

Fig. 1. Chemical structure of curcumin.

The aim of this study was to investigate the effectiveness of pure curcumin as organic corrosion inhibitor for carbon steel (C.S) in seawater solution at temperature range (298 - 328 K) using Potenstatic measurements.

II. EXPERIMENTAL PART

2.1. Chemicals and Materials

Carbon Steel (C.S) was used as metallic materials with chemical Composition as described in the table 1.

Many chemical were used in this work include some regents which are listed in table 2 with their purity and origin.

TABLE 1 :Chemical composition for C.S(45).

Grade	*% C*	*% Si*	*% Mn*	*%S*	*% P*	*% Ni*	*% Cr*	*%Mo, Cr+Ni*	*%Fe*
C45	0.42-0.50	<0.40	0.50-0.80	<0.045	<0.045	0.40	<0.40	<0.10	97.31-97.69

TABLE 2: Chemical materials used in this study.

Raw Material	*Molecular Formula*	*Supplier*	*Purity*
Distilled Water	H_2O	University of Baghdad/College of Science.	high degree of purity/empty of additional
Dimethyl sulfoxide (DMSO)	C_2H_6OS	CDH	99.5%
Sodium Chloride	NaCl	MERCK	99.5%
Pure Curcumin	$C_{21}H_{20}O_6$	Fluka	98%

2.2. Preparation of Specimen

A piece of carbon steel (C45) of (0.5 mm) thickness was mechanically cut into circular sample with dimensions of 2.5 cm in diameter then: Carbon steel sample surface was polished with silicon carbaid paper in different sizes (320,400,800,1000,1200, 1500,2000) until it gain a mirror image shape.Then washed by distilled water and acetone. The Specimen was kept in desiccators for protecting and preventing them from oxidation by atmospheric air and moisture.

2.3. Preparation of the test solution and inhibiting solution

The test solution (3.5% NaCl) was prepared by added 35 g NaCland 20 ml of DMSO than complete the volume to 1 litter by distilled water.

The inhibiting solution of four concentrations ($2.7*10^{-6}$,$1.3*10^{-5}$,$2.7*10^{-5}$,$3.2*10^{-5}$M) of pure curcumin were prepared by dissolving 0.012 g of pure curcumin in 20 ml of DMSO and complete the volume to 1 litter by distilled water in order to prepare stock solution ($3.2*10^{-5}$ M), then prepare ($2.7*10^{-5}$, $1.3*10^{-5}$, $2.7*10^{-5}$ M) pure curcumin from the stock solution with the same percentage of DMSO and complete the volume to 1 litter by distilled water.

2.4. Electrochemical Measurements

In this technique three electrode corrosion cell was used, in which the working electrode is carbon steel (type:C45), the reference electrode is the standard Calomel electrodeand the auxiliary electrode is platinum electrode. The electrochemical system consists of potentiostate device (Germany, Mlab 2000), corrosion cell (1000 mL) and electrodes with a computer and MLabSci software were used for data acquisition and analysis [13]. And finally it consist of water bath to control the temperature.

To determine the open circuit potential (OCP) of the specimens, the specimens have been immersed in

seawater solution (3.5% NaCl and DMSO) in different temperatures (298, 308, 318 & 328K) to reach the steady state between the specimen material and electrolytic solution. The change in potential according to the current were determined during (15 min.), and time step equal to 60 seconds for each specimens. After reaching the steady state condition, the determined potential is known as corrosion potential or free potential or open circuit potential.

III. RESULTS AND DISCUSSION

3.1. Potentiostatic polarization measurements

Anodic and cathodic polarization curves for the corrosion of Carbon steel in seawater solutionwithout and with different concentrations of pure curcumin at temperature range of (298-328K) is shown in (figure 2).

The extrapolation method for the polarizations curves was applied and the data of corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafel slopes (b_c and b_a) and percentage inhibition efficiency (%I) are listed in (table 3).

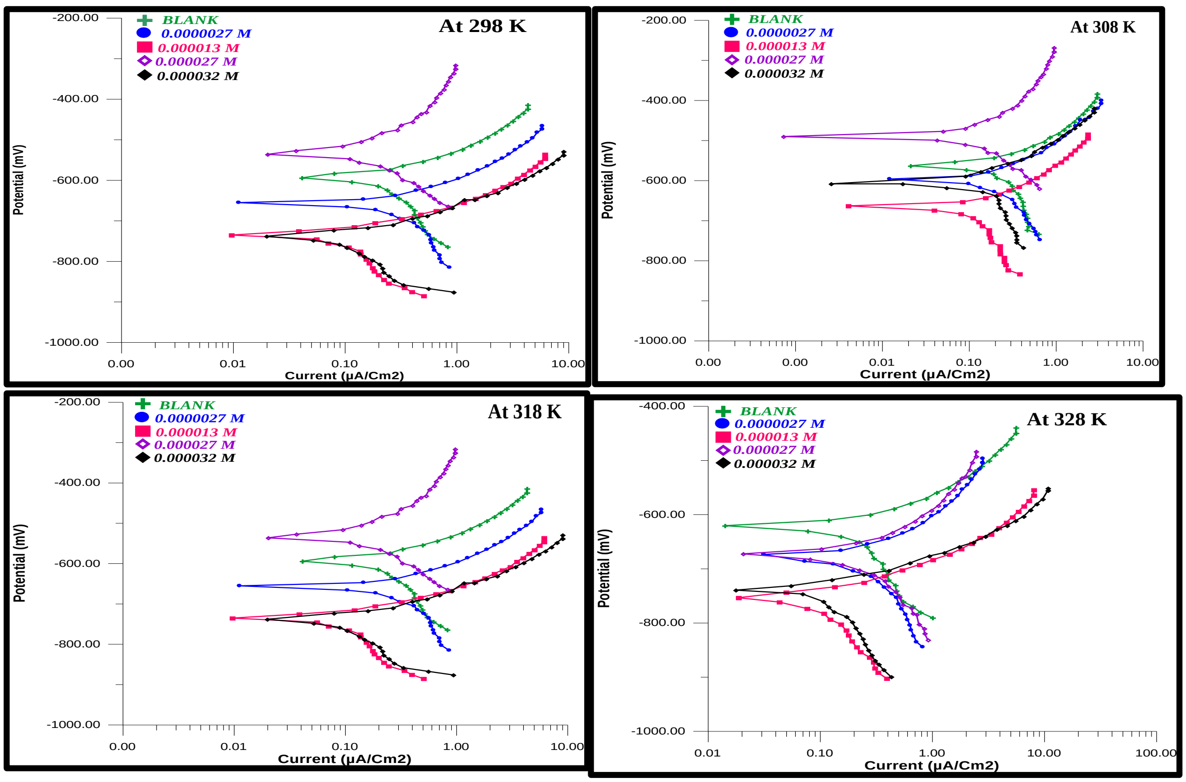

Fig. 2. Polarization plots of C.S corrosion in NaCl model system for various concentrations of pure curcumin at temperature range 298-328K.

Inhibition efficiency (%I) can be determine using the following equation[14]:

$$\%I = \frac{i - i_{in}}{i} \times 100 \qquad (1)$$

Where iand i_{in} are the corrosion current densitiesin the absence and presence of the inhibitor, respectively.

As shown in (figure 2) the addition of different inhibitor concentrations effects on both anodic and cathodic region of the Tafel curves, and decreases both the anodic and cathodic current densities.

The polarization resistance (R_P) may best determined from the following equation [14].

$$R_p = \frac{d(\Delta E)}{di} = \frac{b_a b_c}{2.303\,(b_a + b_c)\, i_{corr}} \qquad (2)$$

Where E and E_{corr} are in mV, i_{corr} in $A.cm^{-2}$, ba, bc are in $V.dec^{-1}$ and R_P in $\Omega.\ cm^2$.

Table 3 shows a decrease in corrosion current density (i_{corr}) with the addition of the inhibitor. The values of corrosion current density increased with temperature increased and decreased with inhibitor

concentration increased up to $2.7*10^{-5}$M then with increasing inhibitor concentration than $2.7*10^{-5}$M the corrosion current density will be increased. The opposite of corrosion current density is the inhibition efficiency, the best inhibition efficiency obtained with $2.7*10^{-5}$ M pure curcumin concentration at 298K that equal to (77.5%).

In general the data in table 3 show that increasing temperature shifts the values of corrosion potential in cathodic direction (the metal/alloy become more active). The increasing of negative value of corrosion potential in the presence of inhibitor compared to its absence indicate that the inhibitor made the metal/alloy more active toward corrosion except at $2.7*10^{-5}$M it will be more noble at temperature below 328K.

The obtained results show that the best R_p value appeared at 298K of $1.3*10^{-5}$ M pure curcuminsolution.

TABLE 3. Corrosion data of C.S corrosion in NaCl model system in the absence and presence of different pure curcumin concentrations at temperature range 298-328K.

Pure Curcumin / M	T/K	i_{corr}/μA.cm^{-2}	E_{corr}/ mV	b_c/mV.dec^{-1}	b_a/mV.dec^{-1}	w.l/ g.m^{-2}.dl^{-1}	P.L/ mm.y^{-1}	R_p/Ω.cm^2	θ	IE%
Blank	298	99.61	-498.6	-146.3	128.3	24.9	1.16	297.97	-	-
	308	129.63	-564.6	-124.5	80.2	32.4	1.5	163.39	-	-
	318	168.47	-595.5	-195.4	84.8	42.1	1.96	152.42	-	-
	328	185.45	-621.2	-262.5	77.3	46.4	2.15	139.82	-	-
$2.7*10^{-6}$	298	62.97	-526.4	-81.8	59.4	15.7	0.731	237.29	0.368	36.78
	308	84.01	-597.1	-96	62.8	21	0.975	196.23	0.352	35.19
	318	121.66	-655.1	-95.5	53.2	30.4	1.41	121.94	0.278	27.78
	328	148.21	-674.2	-158.9	69.8	37.1	1.72	142.083	0.201	20.08
$1.3*10^{-5}$	298	38.63	-547.6	-99.5	79.6	9.66	0.448	497.07	0.612	61.22
	308	65.28	-664.1	-145.4	60.5	16.3	0.758	284.18	0.496	49.64
	318	88.49	-736.6	-247.3	70.5	22.1	1.03	269.2	0.475	47.47
	328	102.44	-753.1	-281.5	69.1	25.6	1.19	235.17	0.448	44.76
$2.7*10^{-5}$	298	22.41	-454.9	-61.4	43.8	5.6	0.26	495.33	0.775	77.5
	308	52.88	-492.4	-70.6	88.9	13.2	0.614	323.12	0.592	59.21
	318	75.38	-536.1	-74.7	109.4	18.8	0.875	255.7	0.553	55.26
	328	92.11	-673.5	-78.3	63.2	23	1.07	164.86	0.503	50.33
$3.2*10^{-5}$	298	39.09	-534.1	-60.7	47.1	9.77	0.454	294.6	0.608	60.75
	308	56.36	-609.3	-68.5	75.7	14.1	0.654	277.05	0.565	56.52
	318	78.63	-739.2	-181.1	60.2	19.7	0.913	249.5	0.533	53.33
	328	100.65	-738.7	-238.9	62.5	25.2	1.17	213.72	0.457	45.73

3.2. Kinetic and Thermodynamic Studies

Thermodynamic parameters play an important role in studying the corrosionprotection mechanism.The equation used to calculate the activation parameters of the corrosion process is similar to Arrhenius (equation 3). Moreover, transition state
(equation 4) were used [15].

$$\mathbf{Log(I_{corr}) = Log\ A - \frac{E_a}{2.303\ R\ T}(3)}$$

$$\mathbf{Log(I_{corr}/T) = Log\ (K/h) + \frac{\Delta S^*}{2.303R} - \frac{\Delta H^*}{2.303RT}(4)}$$

Where i_{corr} is corrosion current density, E_a is the apparent activation energy, R is the universal gas constant (8.314 J mol^{-1}.K^{-1}), T is temperature in Kelvin, A is the Arrhenius pre-exponential factor, h is the Plank's constant (6.626 x 10^{-34} J.s), N is the Avogadro's number (6.022 x 10^{23} mol^{-1}), K is the Boltzmann constant, ΔH* is the enthalpy ofactivation and ΔS* is the entropy of activation. The apparent activation energy (E_a) at optimum concentration of pure curcumin wasdetermined by linear regression between log I_{corr} and 1/T (figure.3) and the result is shown in table. 4.

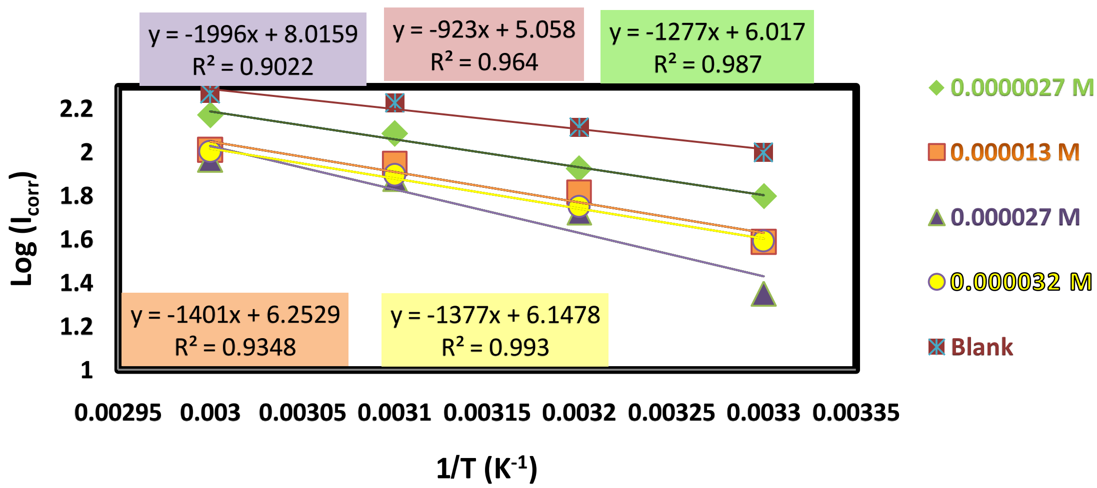

Fig. 3. Plot of log I_{corr} versus 1/T for the C.S corrosion in NaCl model system containing various pure curcumin concentrations.

Straight lines were obtained from the plots of log I_{corr}/T vs. 1/T, which are shown in (figure 4). With the slope of ($-\Delta H^*$/2.303 R) and an intercept of[(log (R/Nh) +(ΔS^*/2.303 R)] from which the values of ΔH^* and ΔS^*, respectively were calculated.

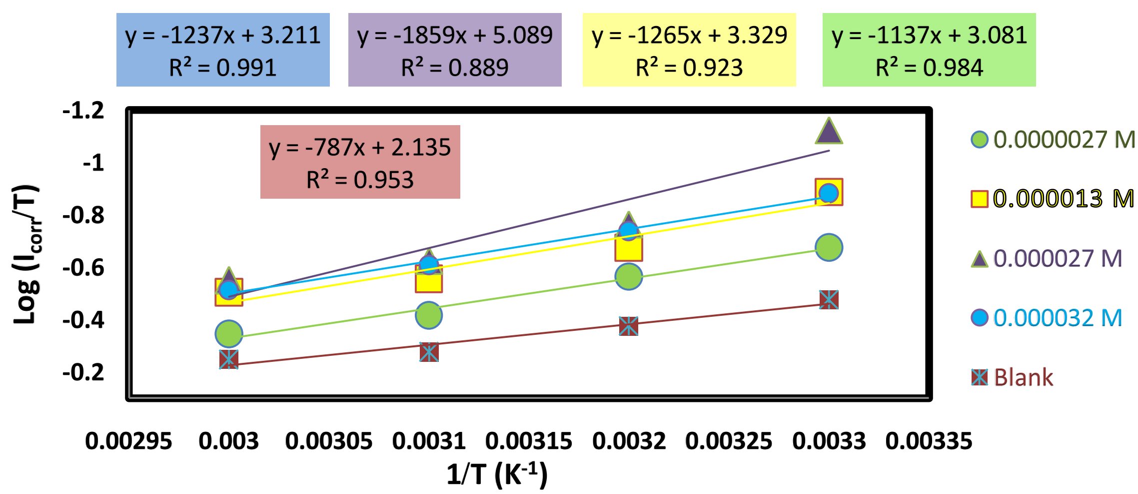

Fig. 4. Plots of log I_{corr} /T vs. 1/T for the corrosion of C.S in NaCl model system in the absence and the presence of different pure curcumin concentration.

The kinetic and thermodynamic quantities are listed in (table 4). The values of activation energy in the presence of the inhibitor are higher than for case in the absence of it, and the largest value indicated at $2.7*10^{-5}$M of pure curcumin concentration that equal to (38.218) kJ.mol^{-1}.

The positive value of ΔH for corrosion processes in the presence and absence of inhibitor reveal the endothermic nature of the carbon steel dissolution process.

Values of ΔS in presence of pure curcumin inhibitor are generally lower than the case without adding inhibitor.

The Gibbs free energy (ΔG) for the corrosionof carbon steel inNaCl model system for uninhibited and inhibited carbon steel increase with increasing temperature.

TABLE 4: Activation parameters Ea, ΔH* and ΔS* for the C.S dissolution in NaCl model system in the absence and the presence of pure curcumin concentrations solutions.

Pure Curcumin/ M	T/K	$1/T/K^{-1}$	i_{corr}/μA.cm^{-2}	Logi_{corr}	Log (i_{corr}/T)	-ΔG/ kJ.mol^{-1}	ΔH/ kJ.mol^{-1}	-ΔS/ J.K^{-1}.mol^{-1}	Ea/ kJ. mol^{-1}	A Molecules. cm^{-2}.S^{-1}
Blank	298	0.0033	99.61	1.998	-0.476	61.855	15.069	156.7	17.673	$6.89*10^{28}$
	308	0.0032	129.63	2.113	-0.376	63.425				
	318	0.0031	168.47	2.226	-0.276	64.995				
	328	0.0030	185.45	2.268	-0.247	66.565				
$2.7*10^{-6}$	298	0.0033	62.97	1.799	-0.675	62.894	21.77	138.6	24.451	$6.27*10^{29}$
	308	0.0032	84.01	1.924	-0.564	64.274				
	318	0.0031	121.66	2.085	-0.417	65.654				
	328	0.0030	148.21	2.171	-0.345	67.034				
$1.3*10^{-5}$	298	0.0033	38.63	1.587	-0.887	64.153	24.221	133.8	26.825	$1.08*10^{30}$
	308	0.0032	65.28	1.815	-0.674	65.493				
	318	0.0031	88.49	1.947	-0.555	66.833				
	328	0.0030	102.44	2.01	-0.505	68.173				
$2.7*10^{-5}$	298	0.0033	22.41	1.35	-1.124	65.397	35.597	100.1	38.218	$6.25*10^{31}$
	308	0.0032	52.88	1.723	-0.765	66.397				
	318	0.0031	75.38	1.877	-0.625	67.397				
	328	0.0030	92.11	1.964	-0.551	68.397				
$3.2*10^{-5}$	298	0.0033	39.09	1.592	-0.882	64.213	23.685	136.1	26.366	$8.46*10^{29}$
	308	0.0032	56.36	1.751	-0.737	65.573				
	318	0.0031	78.63	1.895	-0.607	66.933				
	328	0.0030	100.65	2.003	-0.513	68.293				

3.3. Adsorption isotherm behavior

The adsorption isotherm was determined by assuming that inhibition effect is due mainly to the adsorption at metal/solution interface. Adsorption isotherm provided basic information on the adsorption of inhibitors on the metal surface. The fractional surface coverage values (θ) is used as a function of inhibitor concentration must achieve. The values of θ can easily be determined by the ratio %IE/100, where %IE is inhibition efficiency obtained by potentiostat method, so it is necessary to determine empirically which isotherm fits best to the adsorption of inhibitors on the C.S surface. Several adsorption isotherms (viz., Frumkin, Langmuir, Freundlich, Temkin), were tested, and the Langmuir adsorption isotherm provides the best description of the adsorption behavior of this inhibitor.

The following equation gives the Langmuir isotherm. [16]:

$$\mathbf{C/\theta = \frac{1}{K_{ads}} + C} \quad \textbf{(5)}$$

Where C is the inhibitor concentration, K_{ads} is the equilibrium constant of the adsorption process, and θ is the surface coverage. The Plot of C/θ Vs. C well yields a straight line(figure 5) with regression coefficient (R^2) almost equal to 1. This suggests that pure curcumin in the present study obeyed the Langmuir isotherm.

TheValues of the enthalpy, entropy of adsorption process had been determined from the followingequation:

$$\mathbf{Log\ K_{ads} = \frac{-\Delta H_{ads}}{2.303RT} + \frac{\Delta S_{ads}}{2.303R} + Log\ \frac{1}{55.55}} \textbf{(6)}$$

The value 55.55 in the equation above is the concentration of water in solution in mol. L^{-1}.

From the values of ΔS_{ads} and ΔH_{ads}, the free energy of adsorption was calculated using the following equation:

$$\mathbf{\Delta G_{ads} = \Delta H_{ads} - T\ \Delta S_{ads}} \textbf{(7)}$$

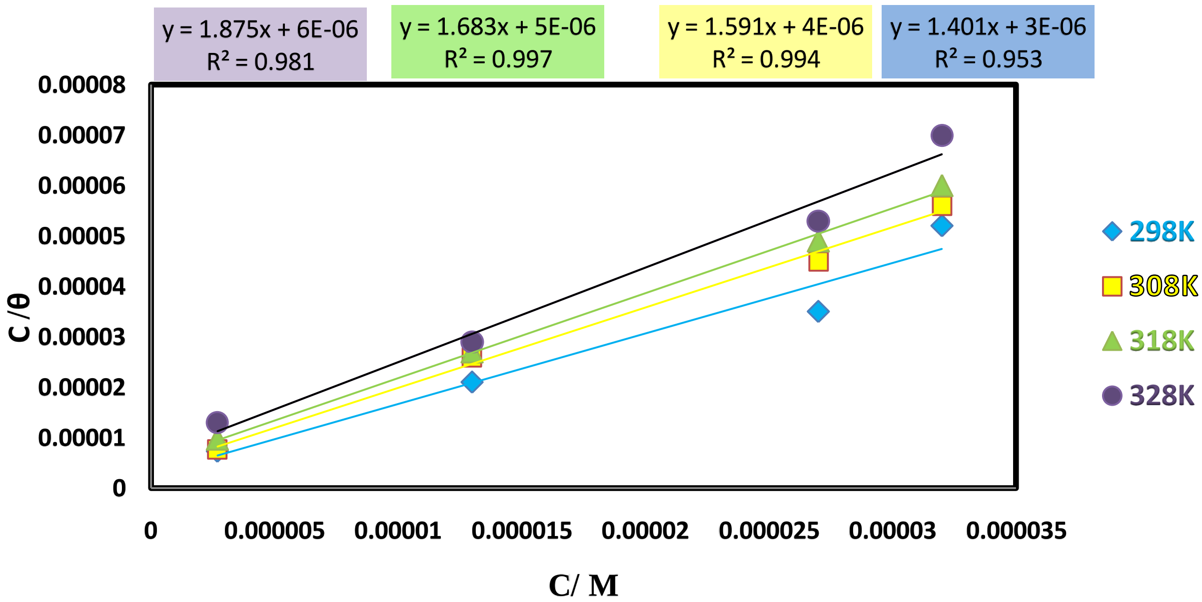

Fig.5. Langmuir isotherms plots for the adsorption of pure curcumin on (C.S.) at different temperature.

The thermodynamic parameter from adsorption process was listed in table 5:

TABLE 5:Adsorption parameter for the adsorption of pure curcumin on the surface of C.S.

T/K	K_{ads}/ M^{-1}	$\Delta G/kJ.mol^{-1}$	$\Delta H/kJ.mol^{-1}$	$\Delta S/kJ.mol^{-1}.K^{-1}$	R^2
298	333,333.33	-41.795			0.9535
308	250,000	-42.555			0.9948
318	200,000	-43.315	-19.147	0.076	0.9977
328	166,666.67	-44.075			0.9819

The slope of variation of log (K_{ads}) vs. 1/T = ($-\Delta H_{ads}$ / 2.303R) , So ΔH_{ads} = -19.147 kJ.mol^{-1} (figure 6).A negative value of the ΔH_{ads} indicated that the adsorption process of inhibitor is an exothermic process, In an exothermic process physisorption is distinguished from chemisorption by considering that an exothermic value of a physisorption process is lower than -40 kJ.mol^{-1} while the adsorption heat of chemisorption process approaches -100 kJ mol^{-1}. In this study the standard adsorption heat is ΔH°_{ads} = -19.147 kJ.mol^{-1} postulates that is physisorptionmore favored.

The negative value of the free energy of adsorption indicate a spontaneous adsorption of these inhibitors on C.S surface and increase as thetemperature increase.

The values of adsorption constant shows in (table 5) are decreases with temperature increases, and the highest value obtained at 298K.

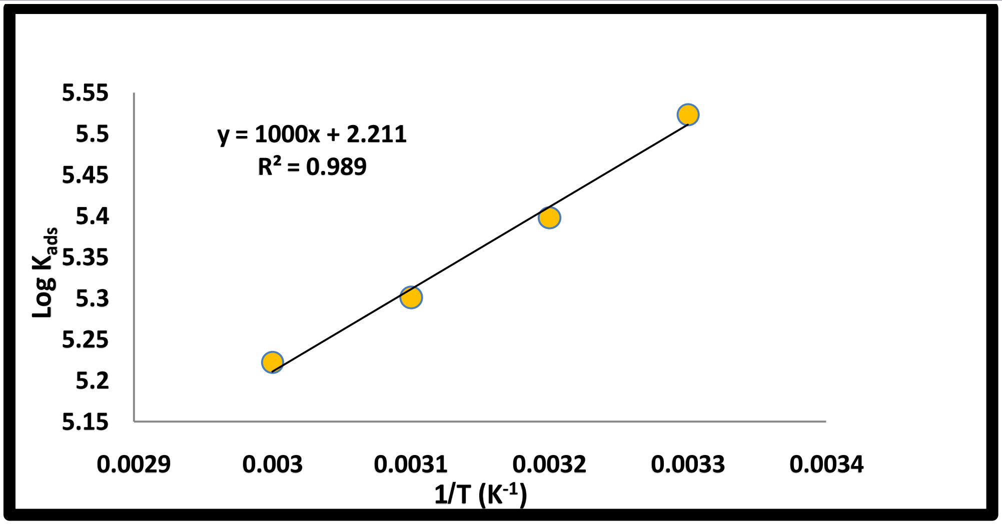

Fig.6.Plot of log K_{ads} versus 1/T.

IV. CONCLUSIONS

The inhibition efficiency decrease with temperature increase at all pure curcumin inhibitor concentrations and increase with inhibitor concentrations increase up to $2.7*10^{-5}$M then with increasing inhibitor concentration than $2.7*10^{-5}$M the inhibition efficiency will be decrease.The best inhibition efficiency obtained with $2.7*10^{-5}$ M pure curcumin concentration at 298K which reach to 77.5%.

The best R_p value obtained with $1.3*10^{-5}$ M pure curcumin concentration at 298K that equal to 497.07 $\Omega.cm^2$.
The positive value of ΔH^* for corrosion processes in the presence and absence of inhibitor reveal the endothermic nature of the carbon steel dissolution process.
The Gibbs free energy (ΔG) for corrosion of carbon steel in NaCl model system for uninhibited and inhibited carbon steel increase with increasing temperature.

The inhibition of C.S in NaCl model system by pure curcumin inhibitor obey the Langmuir adsorption isotherm.The inhibition were physisorptionin nature with an exothermic adsorption process.The negative value of the free energy of adsorption indicate a spontaneous adsorption of pure curcumin inhibitor on C.S surface.

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